OPTIMIZATION OF GAS CHROMATOGRAPHY – MASS-SPECTROMETRY PARAMETERS FOR PETROLEUM ANALYSIS

Dr. Mereke Alimzhanova

Meuyert Sergazina

Makpal Yelemessova

Kazhybek Ashimuly

Center of Physical Chemical Methods of Research and Analysis, al-Farabi Kazakh National University, **Republic of Kazakhstan**

ABSTRACT

Study of the component composition of petroleum is one of the most difficult task of analytical analysis, since the composition of the oil is extremely complex, and the content of the individual components in the mixture varies from deposit to deposit. Nowadays, gas chromatography mass - spectrometry (GC/MS) is a powerful tool for chemical characterization of petroleum and petroleum products. Present paper describes optimization of GC/MS parameters for petroleum analysis. Type of column, injector temperature, volume of injection of sample and split ratio were optimized. In the results of selecting efficient column, non - polar type of column was selected as more efficient tool for the separation of a petroleum hydrocarbon groups. In addition, the injector temperature 200 °C was the optimal injector temperature, which provides the maximum signal response of petroleum hydrocarbons. The optimal sample injection volume was 0.5 µL in chosen value of split ratio of 50:1. Due to the optimized parameters, the component composition of petroleum from western and southern regions of Kazakhstan was determined. Thus, the proposed optimization parameters are necessary for further development of method of determination of fractional and component composition of petroleum by GC/MS.

Keywords: petroleum; optimization; component composition; gas chromatography; mass – spectrometry.

INTRODUCTION

Petroleum is found in huge quantities below the surface of the earth and petroleum products are used as fuels and as raw materials in the chemical industries. Petroleum consists primary of organic hydrocarbons of various molecular weights including alkanes, naphthalenes and aromatics and heteroatom compounds. In the standard methods, the component composition of petroleum and petroleum products are determined after the separation to fractions by different methods including GC/FID, HPLC [1-3]. Current methods of analysis of petroleum can not give detailed component composition fully and require a lot of labors. GC/MS is a powerful tool for the analysis of heavy and volatile substances such as petroleum and petroleum products. The selection of column is very important step in the analysis, it is necessary to provide better and more efficient separation of the mixture components, especially such a complex as petroleum. Non - polar capillary columns, such as, ZB-5MS, HP-PONA and DB-5MS used to define the component composition of petroleum [4 - 7].

The major function of gas chromatograph inlet provides accurate, reproducible, and predictable introduction of sample into the column. Knowledge of the temperature of the component composition of petroleum is very important to adjust the parameters of GC/MS and choose the optimum temperature for the injector. In the studies of analyzing of petroleum by GC/MS were used injector temperature in the range 250 - 300 °C [8 - 12]. And for petroleum of Kazakhstan petroleum field these parameters were not optimized. Therefore, optimization parameters of GC/MS for analysis of petroleum of Kazakhstan are relevant. A main goal of this study was to explore GC/MS through the optimization of the column and injection parameters of GC/MS applied to the analysis 6 different representative petroleum of Kazakhstan.

EXPERIMENTAL PART

Chemicals: Chloroform (> 99.8 %, Sigma-Aldrich, USA).

Four samples of petroleum: “Balgymbayev”, “Baichunas”, “Kosshagyl”, “Zhanaozen” were obtained from west part of Kazakhstan. Petroleum sample “Nurali” was obtained from south part and “Kumkol” was obtained from north part of Kazakhstan.

For analysis, 0.10 g of each sample of petroleum was dissolved in chloroform (> 99.8 %, Sigma-Aldrich, USA) using 10 mL volumetric flask. There was prepared a solution with a concentration of 10 mg L^{-1}. From the resulting solution was selected an aliquot volume of 1 mL which placed in a vial, and then analyzed by GC/MS (Agilent, USA) system. The temperature of the ion source and the quadrupole mass spectrometer detector was 150 and 230 °C, respectively. Solvent delay was 4 min. Analysis of each sample was performed in two parallels.

Study the effectiveness of type of column in petroleum analysis

In this study were tested two kinds of columns of semi-polar and non-polar types of different marks: J&W DB-35MS (Agilent, USA) and Phenomenex ZB-5 (Zebron, USA).

Optimization of temperature of injector

For analysis, the samples were taken from “Kosshagyl” and “Kumkol” oil-fields. They have significant differences between them, such as the fractional and component composition. Petroleum from the petroleum field “Kosshagyl” is characterized by an almost complete absence of paraffins and low gasoline fractions, whereas the petroleum from “Kumkol” is lighter and less oily.

Optimization of sample injection volume

Optimization was performed by selecting the optimum volume of sample injected to ensure sufficient sensitivity. For the analysis, petroleum was selected from the petroleum field “Nurali”, in which noted a clear predominance of n-alkanes. The volume of injected sample of petroleum ranged: 0.2 μL; 0,5μL; 1.0 μL.

Optimization of split ratio of the sample injection

Optimization was performed by selecting the optimal split ratio for the input samples to provide sufficient sensitivity GC/MS. For the analysis, petroleum was selected fromv"Nurali" oil field. Splitless mode (split) were varied in the following ratios: 20:1, 50:1, 100:1, 200:1, 500:1.

RESULTS AND DISCUSSION

Study the effectiveness of type of column in petroleum analysis

In an experiment using various types of columns – (№1 and №2) were obtained chromatograms, which were subsequently processed according to individual ions of the following compounds: paraffins, benzenes, naphthalenes, acenaphthenes, fluorenes, phenanthrenes. The results of the data presented in Table1.

Table 1. The results of analysis obtained by using different column

Peak Area, $\times 10^{-6}$ (a.u.)							
Compound	Type of column	“Balgymbayev”	“Nurali”	“Baichunas”	“Kumkol”	“Kosshagyl”	“Zhanaozen”
Paraffins (m/z 57)	1	6,06	11,84	4,25	13,6	3,72	7,88
	2	30,52	55,49	15,78	104,02	21,28	43,15
Benzenes (m/z 77)	1	0,29	0,11	0,2	0,16	0,32	0
	2	3,42	1,23	2,27	4,22	3,97	0,59
Naphthalenes (m/z 128)	1	0,08	0,17	0,01	0,24	0,08	0,03
	2	1,88	1,03	1,05	3,28	2,4	0,43
Acenaphthenes (m/z 154)	1	0,02	0,17	0	0,29	0	0,13
	2	1,79	1,51	0,74	4,2	1,43	1,27
Fluorenes (m/z 165)	1	0,74	0,07	0,92	0,22	1,17	0
	2	7,4	2,46	5,75	6,66	9,71	2,82
Phenanthrenes (m/z 178)	1	0,03	0,03	0,02	0,02	0,11	0
	2	2,5	0,96	2,12	2,64	3,73	0,95

**Note: 1 – semi-polar column; 2 – non-polar column.*

Chromatograms were obtained during the experiments of column №1 and №2, were superposed on each other for the purpose of visual comparison (Figure 1).

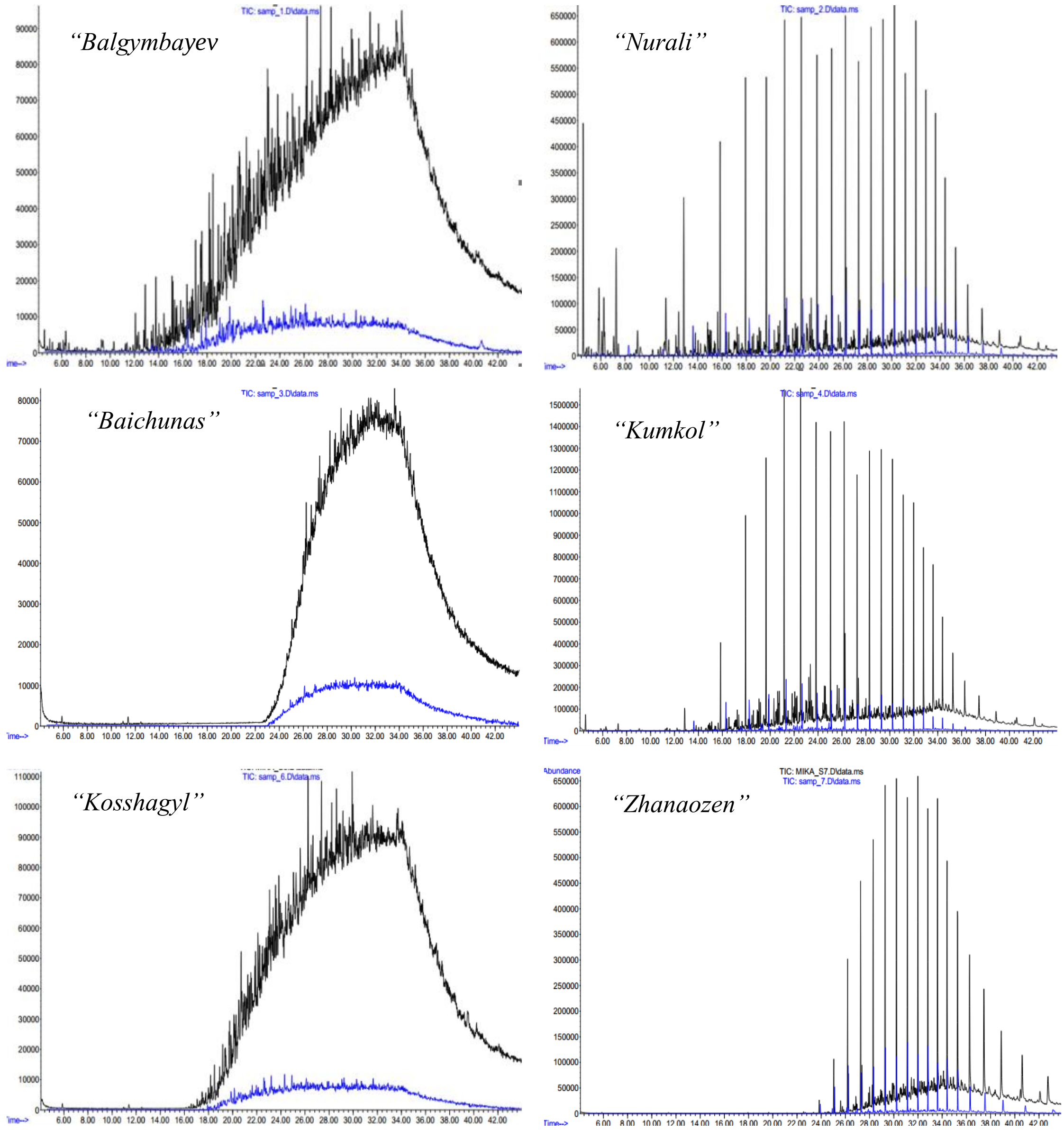

Figure 1. Overlay chromatograms of petroleum samples from different oil-fields by using two types of columns

As seen from the comparison diagram and obtained chromatograms, using column of non-polar type ZB-5 Phenomenex (Zebron, USA) provides a greater response in 6 groups of compounds that are represented paraffins, benzenes, naphthalenes, acetanaphthenes, fluorens and phenanthrenes, compared to the column average polarity J&W DB-35MS (Agilent, USA). Thus, the non-polar type column is more efficient tool for the separation of a petroleum hydrocarbon groups.

Optimization of temperature of injector

After analyzing, the obtained chromatograms were processed and plotted the dependence of response signal of major groups of petroleum hydrocarbons on the temperature of the injector (Figure 2). It has been found that the temperature significantly influences both the separation of the petroleum components, and the hydrocarbon response signal. The maximal signal response of petroleum hydrocarbons of petroleum fields “Nurali” was observed at injector range 150 - 200 °C, while the standard deviation of the sample for given values of temperature was minimal, indicating a high reproducibility of parallel analyzes. At higher temperatures decrease the response signal, which can be caused by thermal destruction of the joints and structural changes in their composition.

It is also found that the retention time is sensitive to the temperature of device of sample introduction and it decreases with an increase of temperature. This is clearly seen in the imposition of chromatograms. Thus, the sample injection temperature is 200 °C was selected as optimum for maximum signal response of the sample components.

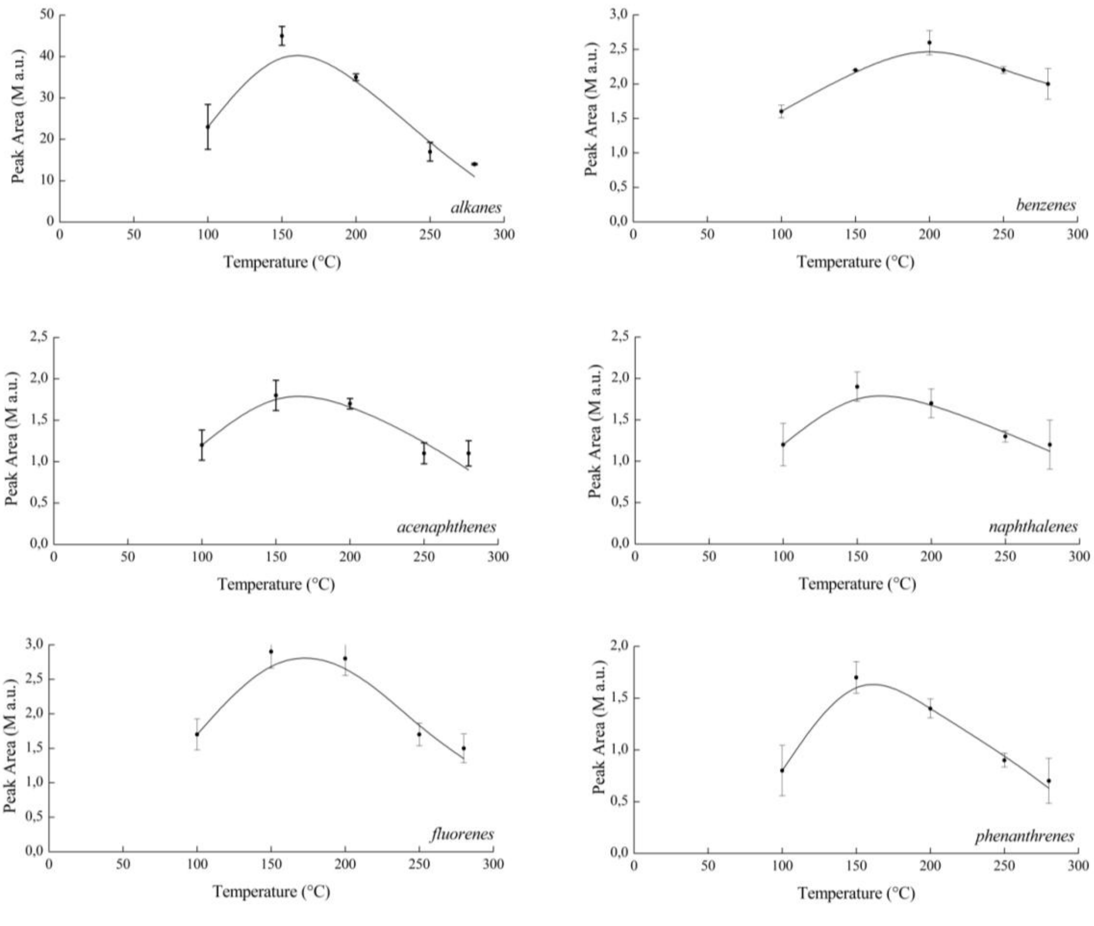

Figure 2. Dependence graph of response signals of groups of petroleum hydrocarbons in petroleum field “Nurali” on temperature of the injector

Optimization of sample injection volume

After analyzing the obtained chromatogram were processed. According to the obtained results, with an increase in the volume of sample injection response signal increases in direct proportion, as evidenced by the magnitude-squared, which is close to unity. According to the results as the optimum volume of sample injection should choose the maximum value for obtaining maximum signal response. By increasing the sample volume to 1.0 μL, sensitivity was reduced, which may be caused by the fact that was overload mass spectrometric detector. Thus, the optimal sample injection volume was 0.5 μL.

Optimization split ratio of the sample injection

After analyzing, the obtained chromatograms were processed and plotted the dependence of response signal of n-alkanes (m/z 57) on the ratio splitless injector (Figure 3).

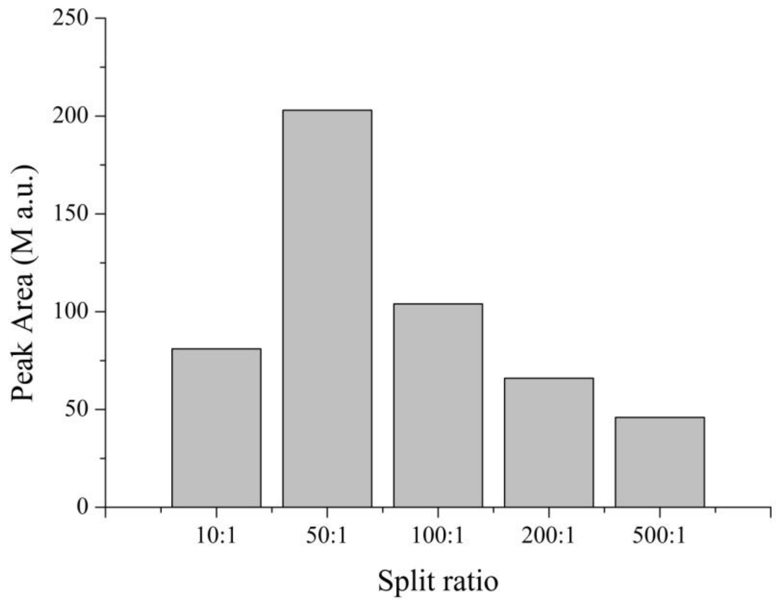

Figure 3. Dependence graph of the response signal of n-alkanes of petroleum from "Nurali" on the value of split ratio of the injector

At the same time there are minor differences in the signal intensity at values of split ratio of 200:1 and 500:1. Reducing the response signal corresponds to a reduction of the amount of substance which goes into the detector. However, the observed nonlinear, but the power dependence may be due to the fact that an increase in the division of flow into the system gets an extremely small amount of a substance consisting mainly of light hydrocarbons, and the heavy hydrocarbons do not have time to equilibrate and enter the system during opening and closing of valves streams. With decreasing values of split ratio (with the increase number of misses the detector substance) petroleum components more time to move from the evaporator to the column. Thus, the recommended value of split ratio was chosen 50:1, provided the dissolution of petroleum (stock solution preparation for analysis) in a solvent in a ratio of 50:1 to avoid contamination of the sample introduction device and to achieve the required sensitivity.

CONCLUSION

The knowledge of major composition components of petroleum is needed in various fields in the petroleum industry such as studies related to processing and environmental effects. GC/MS is a powerful tool in this area and provides accurate identification of the petroleum composition. There are no studies to optimize to GC/MS parameters for petroleum of Kazakhstan. In this work the main parameters of GC/MS were optimized – type of column and injection parameters. In addition, six different types of petroleum were analyzed to optimize parameters of GC/MS. By the results the composition components of petroleum of Kazakhstan were determined. This optimized method is fast, repeatable and can be used to develop methods for determination the component composition of petroleum based on GC/MS, which may be used in the petrochemical industry, for evaluation and quality control of exported Kazakh oil, for environmental monitoring. However, this optimized method can be used for the organization of environmental monitoring in the oil-producing regions, for the study of the behavior of petroleum hydrocarbons in the environment and for the development of effective methods of control over remediation and restoration of contaminated areas.

ACKNOWLEDGEMENTS

This work was conducted under the project *“Development of the methods for fast determination of the fractional and component composition of crude oil and petroleum products based on gas chromatography – mass – spectrometry and comprehensive two – dimensional gas chromatography”* funded by the Ministry of Education and Science of Kazakhstan. Research on this subject was carried out in DPE “Center of Physical Chemical Methods of Research and Analysis”, al-Farabi Kazakh National University.

REFERENCES

[1] GOST 11851-85 Petroleum. Method of determination of paraffins, Kazakhstan, 1986, pp 13.

[2] GOST R EN 12916:2006 Petroleum products. Determination of type of aromatic hydrocarbons in middle distillates, Kazakhstan, 2009, pp 13.

[3] GOST 13379-82 Petroleum. Determination of C_1-C_6 hydrocarbons by GC method, Kazakhstan, 1983, pp 8.

[4] R.James., Gasson., T. Bart., G. Genov., Journal of Petroleum Science and Engineering, Norway, vol. 102, pp 66-72, 2013.

[5] A.Akinlua., T.R.Ajayi., B.B. Adeleke., Organic and inorganic geochemistry of northwestern Niger Delta oils, Geochemical Journal, Nigeria, vol. 41, pp 271 – 281, 2007.

[6] E.O. Odebunmi., R.O Ismaeel., GC-MS characterization of the aromatic fractions of Gulf heavy crude oil sample, IJCBS, Nigeria, pp 42-46, 2013.

[7] M.D. Auria., R. Racioppi., V. Velluzz., A Comparison of Results Obtained Using Liquid Injection and Headspace Solid-Phase Microextraction for Crude Oil Analysis by GC with Mass Spectrometer Detection, Journal of Chromatographic Science, Italy, vol. 46, p 35, 2008.

[8] S. Nasir., N. Mansir., N. M. Augie., Geochemical Study of Crude Oil Samples to Evaluate Extent and Effect of Secondary Alteration Process (i.e. Biodegradation), International Journal of Scientific and Research Publications, Nigeria, vol. 4/issue.10, pp 35-36, 2014.

[9] V. Dhole., M. Narkesari., High Temperature Simulated Distillation According to ASTM D6352 using a Dedicated GC Analyzer, Thermo Fisher Scientific, Nasik, India, pp 10-13, 2008.

[10] M. Kurniawan., K. Mulia., C. Anwar., Wax precipitation in crude oil by Coutinho model based on conventional Gas Chromatography, Scientific contribution Oil&Gas, Indonesia, vol.36/issue. 2, pp 75-82, 2013.

[11] C.I. Anyadiegwu., E. Egelle., P. Ikpeka., Suitability of Gas Chromatography Flame Ionization Detector (GC-FID) for fingerprinting reservoir fluids in Mature and Marginal fields of Nigeria Delta, International Journal of Scientific Engineering and Applied Science (IJSEAS), Nigeria, vol.1/ issue. 5, pp 39-41, 2015.

[12] A.Sainbayar., A.V. Vosmerikov., E. Nordov., A.K. Golovko., Study on Individual Hydrocarbon’s Composition of gasoline fraction of Tamsagbulag Oil, Mongolia, J.Korean Ind.Eng. Chem, Mongolia, vol.16/issue 1, pp 21-27, 2005.